

CORROSION PERFORMANCE AND FIELD EXPERIENCE WITH SUPER DUPLEX AND SUPER AUSTENITIC STAINLESS STEELS IN FGD SYSTEMS

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ABSTRACT

A brief description of the process utilized in flue gas scrubbing systems is presented and the corrosion risks are analyzed in relation with the local environments which are supposed to exist in the main parts of the installation.

Then, Uniform and Localized corrosion performance of welded and non welded super-austenitic and super-duplex stainless steels are investigated and compared to nickel base alloys in laboratory conditions simulating actual flue gas desulphurization environments.

The main corrosion determining parameters investigated are pH, chloride and fluoride concentration as well as temperature.

Results gained from these tests were combined to field experience to design materials selection charts taking into account corrosion risks in various zones of scrubbers. Finally, field experience and references are presented.

INTRODUCTION

Energy production using coal or fuel oil boilers generates exhaust gas polluted by sulphur compounds (SO₂, SO₃) and halide species (Cl⁻, F⁻) which have to be treated to avoid the deleterious effects on human health and environment due to sulphuric (H₂SO₄) and hydrochloric (HCl) acid production in air. To achieve that, Flue Gas Desulfurisation (FGD) systems have been installed for about 20 years now mainly in United States of America, later in European countries and more recently in Korea, Taiwan and Thailand.

The most common technology applied in more than 80% of existing installations consists of scrubbing the polluted gas with a slurry of lime Ca(OH)₂ or limestone CaO in water (Wet FGD Process). The aggressive constituents of the raw gas are SO₂, SO₃, HCl and HF but SO₂ is the most concentrated. SO₂ and SO₃ react respectively with Ca⁺⁺ and H₂O leading to sulfate compounds which precipitate as CaSO₄. HCl and HF give CaCl₂ and NaF which remain in the slurry. The chemical composition of the slurry is continuously monitored in order to insure an efficient neutralizing effect. Then the cleaned gas is blown into the atmosphere.

The process generates aggressive conditions in some parts of the FGD Unit which can cause severe corrosion problems ; as a consequence, high corrosion resistant stainless steels have to be selected in order to insure the efficiency of the system .

PROCESS CONDITIONS and CORROSION PROBLEMS

The raw gas produced by burning coal or fuel oil goes through an electrostatic filter in which flying ash is removed. Then, the hot gas (generally 150-200°C/300-390°F) enters the scrubber unit and goes up while it is sprayed by the neutralizing slurry (generally 3 stages).

If the gas is HCl rich, a pre-scrubber unit can be installed to remove this acid before the main scrubbing stage; a mist eliminator is generally placed between the pre-scrubber and the scrubber to reduce gas pollution by wet HCl. When sea water is used to wash the polluted gas, the mist eliminator is compulsory.

The reaction tank where the neutralizing slurry is prepared is placed either at the bottom or near the scrubber ; a pump feeds the spraying system and insures the recirculation . A demister is placed inside the scrubber above the upper spray level in order to remove liquid particles from the clean gas which reduces salt deposits. Then the clean gas is blown into the chimney.

As the clean gas is not completely depolluted, some acid condensates can be produced in the chimney causing some corrosion problems. So, in some cases, the clean gas is reheated in order to minimize such a risk. Moreover, during start-up periods, the polluted gas is generally partly by-passed ; this means that by-pass ducts and the chimney are submitted to very aggressive conditions due to high temperature and acid-rich condensates.

Significant process parameters and their effect on corrosion

In some areas of the scrubber, the efficiency of the neutralisation reaction between the polluted gas phase and the slurry is not perfect leading to local formation of sulfuric acid. This acid, and the chloride and sometimes fluoride species derived from the coal, produce an aggressive environment. Typical analysis for absorber solutions are : $6 < \text{pH} < 3$, 10,000 to 50,000 ppm Cl^- (sometimes more in closed-loop systems) and F^- between 0 and 500ppm. In such conditions, and even if the medium is fluoride free, conventionnal stainless steels like 316L are prone to uniform and localized corrosion.

Moreover, the corrosion risk is enhanced in some parts of the scrubbing system where the gas velocity is low. In these parts, condensates may accumulate and concentrate, and scaling develops. The pH can reach values as low as 1 or even 0 and in the same time, the chloride concentration can increase up to 5 or 10%, and if the coal contains fluorides, the fluoride content can increase up to several thousands ppm. Under scaling, the solution becomes more and more aggressive due to the lack of oxidizing species. In these conditions, uniform corrosion, pitting corrosion and crevice/underdeposit corrosion can appear.

Thus, from a corrosion point of view, one must consider different situations for which the corrosion mechanisms and consequently the corrosivity are different. These situations can be linked with specific locations in the FGD system :

Gas Phase at the entry of the scrubber : when the temperature is higher than the dew-point, condensation is not possible and the corrosion risk is low. Unfortunately, field experience shows that most often, condensation of exhaust gas occurs. The actual chemical composition of the condensates is difficult to evaluate due to complex physical (gas velocity, wall temperature) and chemical effects (mixing of aggressive species like SO_2 , SO_3 , HCl). The most simple hypothesis consists of considering that SO_3 , SO_2 , HCl and HF are fully dissolved in the water contained in the gas ; this permits to calculate a pH value which may be used to evaluate the corrosion risk. This calculation shows that the pH value are very often between 0 and 1 ; moreover, if the slope of the inlet duct is not sufficient or if the flatness of the duct is not perfect, condensates may remain stagnant in certain areas and the local H_2SO_4 concentration may increase up to several percent. Due to the high temperature, the conditions are very aggressive which explain why high Mo containing Ni base alloys have to be selected

Mixing Zone Gas Phase/Liquid Neutralizing Solution : in this part, the hot polluted gas is sprayed with the neutralizing slurry but the mixing of the 2 phases is not perfect everywhere. So, specific areas near the bottom of the absorber can be submitted to condensates or to saturated acid gas with high chloride contents due to the closure of the water circuit.

Slurry Reaction Tank : the slurry is not in itself very corrosive since the pH is generally monitored around 4.5-5.5 but due to closure of water circuits and the composition of some coal grades, the chloride content can be very high and sometimes F^- ions are present. Moreover, erosion by solid sulfate salts produced by chemical reaction between $\text{SO}_2/\text{H}_2\text{SO}_3$ and lime or limestone can depassivate some parts of the tank, mainly the agitators.

CORROSION PERFORMANCE

Materials

Hot-rolled plates of various stainless steels including austenitic, super-austenitic, duplex and super-duplex grades have been tested. Some nickel base alloys were also investigated. Table 1 shows the typical chemical composition of these materials as well as their Pitting Resistant Equivalent (PREN) values which are often utilized as an indication for the localized corrosion resistance.

The mathematical expression generally used is $\text{Cr} + 3.3\text{Mo} + 16\text{N}$, but a modified version taking into account the effect tungsten is proposed in this table, as a result of previous work carried out in CLI-FAFER Research Centre .

Welded samples were also investigated : filler materials and welding processes utilized are indicated in table 3 .

Table 1 - Typical chemical composition of candidate materials										
AISI or UNS	CLI-FAFER Trademark	Average composition (% weight)							Mn	PRENW [1]
		C	Cr	Ni	Mo	Cu	N2	W		
AUSTENITICS										
316 L	ICL 164 BC	0.02	17	12	2.2					24
31725/26	ICL 170 HE	0.02	18	15	4.5		0.15			35
SUPER-AUSTENITICS										
N08 904	UR B6 N	0.02	20	25	4.3	1.5	0.13			36
N08 925/926	UR B26	0.01	21	25	6.4	0.8	0.20			45
31 266	UR B66	0.01	25	22	5.8	1.5	0.45	2	3	55
32 050	SR 50A	0.02	22	21	6.2		0.25			46
31 254	URB25	0.02	20	18	6	0.8	0.20			43
34 565	UR B46	0.02	24	17	4.5	1	0.40		4.5	45
N08 028	UR B28	0.02	27	31	3.5	1				39
DUPLEXES										
31 803	UR 45 N	0.02	22	5.7	2.8		0.16			34
32 205	UR 45 N+	0.02	22.5	6	3.2		0.17			36
32 750	UR 47 N+	0.02	25	7	3.5		0.25			41
32 520	UR 52 N+	0.02	25	7	3.5	1.5	0.25			41
NICKEL BASE ALLOYS										
N 06 625		0.02	21	bal.	9					51
N 10 276		0.01	15.5	bal.	16			4		68
N 06 022		0.015	21.5	bal.	13.5			3		66
[1] $PREN = Cr+3,3Mo+16N$. $PRENW = Cr+3,3(Mo+0,5W) + 16N$ for URB66										

Testing Conditions

Uniform Corrosion Tests : these tests were carried out in H2SO4 solutions at various concentrations. The effect of pollution due to chloride ions (up to 30,000 ppm) was investigated at pH 0.5 and 0 at 60°C/140°F and 80°C/176°F.

Localized Corrosion Tests : Critical Pitting and Critical Crevice Temperature measurements were achieved in 6% FeCl3 solution according to ASTM G48 and G78 tests.

Electrochemical Investigations : polarization curves were carried out in order to investigate uniform and localized corrosion. The effect of a combined pollution by fluorides and chlorides was studied at pH 3 at 60°C/140°F.

The resistance to crevice corrosion was also investigated in a highly concentrated chloride containing media acidified at pH which simulates the local conditions in a crevice or under deposits. The testing temperature was 80°C/176°F. The uniform dissolution at low potential allows to evaluate the crevice propagation risk due to uniform dissolution in the crevice ; the pitting potentiel permits to evaluate the crevice propagation risk due to the development of new pits inside an existing crevice.

Simulated Absorber Slurry Environment : a multi-partner testing programme has been designed and carried out by CC Technologies Laboratories, Inc. using a special set-up [1]. Non welded and welded samples were submitted for one month to a gaseous environment containing 100 ppm SO2 and 5% O2 and wetted by brines containing 10,000, 20,000, 50,000 and 100,000 ppm chlorides acidified at pH 5. The temperature was monitored to 55°C/131°F and 80°C/176°F.

Main Results

Uniform Corrosion : various stainless steels and Ni base materials were tested in pure H2SO4 acid. The iso-corrosion chart showing the maximum temperature at a given H2SO4 concentration for which the maximum corrosion rate is 0.2mm/yr is shown in Fig.1. The concentration range between 0 and 40% is probably the most usefull for use in FGD systems including the inlet ducts and the chimney.

High Mo containing Ni base materials are obviously much more resistant than conventionnal stainless steels ; as an exemple, alloy N06022 is resistant up to about 110°C/230°F in dilute H2SO4 and at 80°C/176°F in 40% acid. In 10% acid, 316L is resistant up to 35°C/95°F while super-austenitic grades are resistant up to 65°C/149°F for N 08926 and 95°C/203°F for S31266. The super-duplex grade 32520 is resistant up to 85°C/185°F.

Such results demonstrate that high Chromium content together with Molybdenum and Copper additions are quite efficient for improving corrosion resistance in H₂SO₄ <40% concentration.

Another series of tests was conducted in chloride containing solutions (up to 30,000 ppm) at pH 0.5 and 0 at 60°C/140°F and 80°C/176°F; such conditions can be encountered in mixing zones of the scrubbing system when the neutralization is not completed. The results are shown in Table 2.

These tests permitted to establish the limiting conditions for each of the grades tested, according to the measured corrosion rate. At pH=0, 25Cr stainless steels (super-austenitic or super-duplex) can be selected at 10,000 ppm Cl⁻ and it is important to stress that 08926 super austenitic is less resistant than 32 520 super-duplex. At 30,000 ppm chlorides, high Mo containing Ni base alloys must be selected.

At pH=0.5, all 6Mo super-austenitic grades with Ni > 22% as well as super-duplex 32520 were found to be resistant at 60°C/140°F while at 80°C/176°F, only Ni base alloys are resistant.

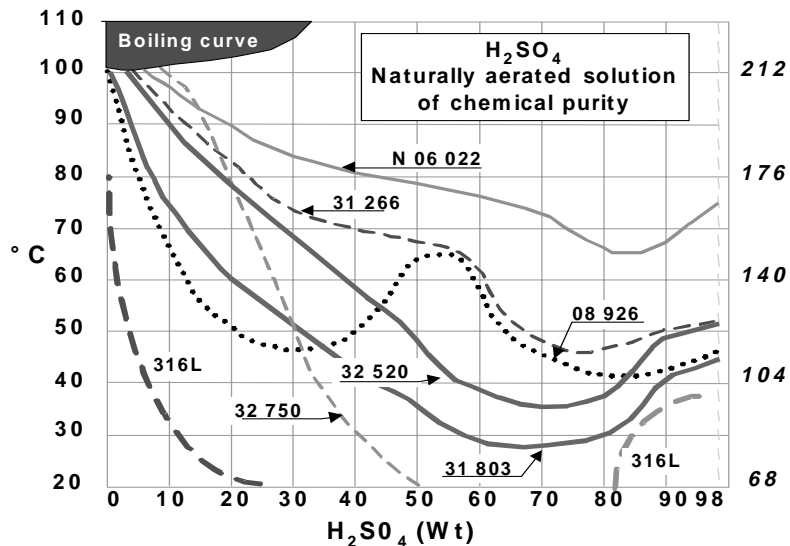


Fig. 1 – Iso-Corrosion diagram (0.2 mm/yr) in H₂SO₄ solutions.

Table 2 - Uniform Corrosion Tests in H₂SO₄ solutions (Corrosion Rate in mm/yr)

	317LNM	8926	31266	32520	N06022	N10276
pH 0, Cl ⁻ free, 60C/140F	0.05	0.02	0.02	0.02	0.02	0.02
pH 0, 10 000 ppm Cl ⁻ free, 60C/140F	2.4	0.5	0.02	0.02	0.02	0.02
pH 0, 30 000 ppm Cl ⁻ , 60°C/140F	6	2.1	0.55	2	0.02	0.02
pH 0.5, Cl ⁻ free, 60°C/140F	0.02					
pH 0.5, 10 000 ppm Cl ⁻ free, 60C/140F	0.02					
pH 0.5, 30 000 ppm Cl ⁻ free, 60C/140F	2.2	0.02	0.02	0.02	0.02	0.02
pH 0.5, 30 000 ppm Cl ⁻ free, 80C/176F		2.5	2.5	1.5	0.02	0.02

Localized Corrosion Tests : Critical Pitting (CPT) and Critical Crevice Temperature (CCT) values measured on hot rolled materials are mentioned in Fig. 2. For each grade, several heats were tested and the data are the minimum values guaranteed. So, individual values are often found to be higher than those indicated in Fig.2.

The ranking for CPT is closely related to the PREN value, whatever the microstructure of the steel; this means that super-duplex grades are quite interesting taking into account the fact that they are less expensive than super-austenitics. The super-austenitic grade 31266 is the most resistant of the tested grades including alloy 625 type. Its CPT value is guaranteed to be much higher than the CPT of the 6 Mo grade 08926; this result is mainly due to the combination of Mo+W+N.

The ranking for CCT is much less related to the PREN_w value, but the 31266 grade remain by far the most resistant ; super-duplex grades 32520 and 32750 were found to be as resistant as the 6 Mo grade 08926.

CCT measurements were also carried out on samples welded in conditions generally utilized for manufacturing industrial vessels. Welding process, filler materials and individual CCT values are mentioned in Table 3.

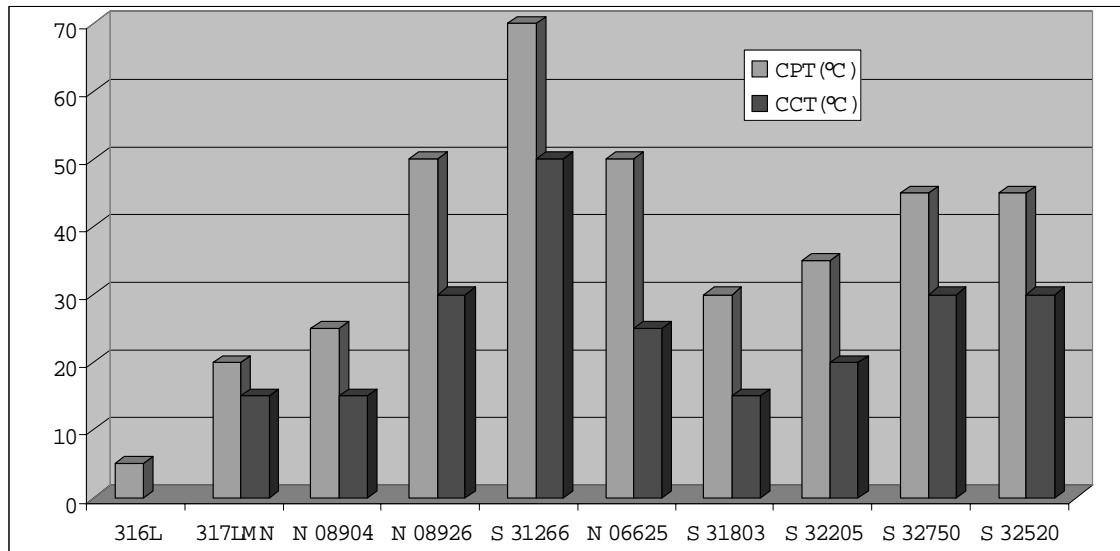


Fig. 2 – Guaranteed values for Critical pitting and Crevice Temperatures in ASTM G48 Tests (6%FeCl3)

From these results, one can conclude that it is necessary to select an over-alloyed filler material in order to obtain a CCT value comparable to that of the base material. This is clearly demonstrated for super-duplex grade 31520 and super-austenitic grade 31266 which exhibit CCT values on samples welded using alloy 22 type (N06022) filler material to be comparable to that obtained on base materials.

On the other hand, the use of 625 type filler material is not recommended for welding Nitrogen containing stainless steels since Nb of the filler may react with nitrogen of the base metal, leading to some detrimental microstructure evolution in the fusion line.

Table 3 – Crevice Corrosion Tests on Welded Samples (ASTM G78)

Grades	Base Material	Welded 1			Welded 2		
		CCT	Filler Mat.	Process	CCT	Filler Mat.	Process
317LMN	22	22	Alloy 625	SMAW			
08926	41	37	Alloy 625	SMAW			
31266	60	60	Alloy 22	SMAW	60	Alloy 22	GMAW
06625	35	35	Alloy 625	SMAW			
06022	85	80	Alloy 22	SMAW			
31803	25	25	25Cr DSS	SMAW			
32520	38	30	25Cr DSS	SMAW	38	Alloy 22	SMAW

Electrochemical Investigations : polarization curves plotted in a 15,000ppm Cl⁻ + 15,000 ppm F⁻ solution at pH=3, 60°C/140°F show that stainless steels may suffer from pitting corrosion (Fig.3). In these conditions the 31254 grade is found to be less resistant than the conventional 6 Mo grade ; this result is mainly attributed to the lower nickel content of 31254.

Another important result is the very good behaviour of the super-duplex grade 32520 which exhibits the same corrosion resistance as the super-austenitic 31266 grade.

Polarization curves were plotted in NaCl 300 g/l, pH=1, 80°C/176°F which simulates the aggressiveness of the medium in regions where crevice corrosion may occur (Fig.4). These conditions are very aggressive so that N08904 suffers from crevice propagation due to uniform corrosion (high activity peak) and to pitting inside the crevice (low pitting potential). N08926 is less prone to crevice propagation due to uniform dissolution but some pitting may occur in the crevice.

The super-austenitic grade 31266 is much more resistant than the previous materials and even better than alloy 625 type ; it is almost as resistant as the Ni base N10276 regarding to pitting while its resistance to crevice corrosion is only slightly lower. This demonstrate that 31266 is much more very resistant than 6 Mo grades to uniform and localized corrosion (crevice and pitting) even in acidic and concentrated chloride containing media.

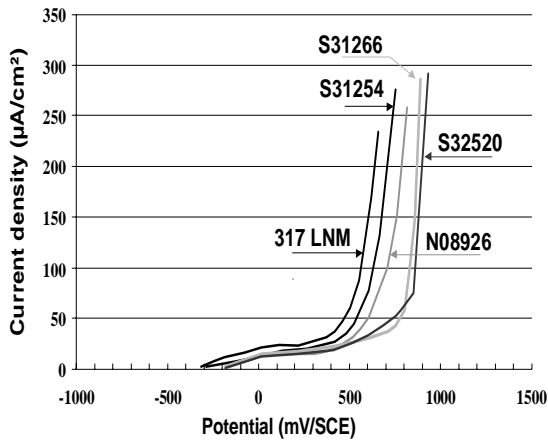


Fig. 3 - Polarization curves in 15,000ppm Cl- + 15,000 ppm F-, pH=3, 60°C/140°F

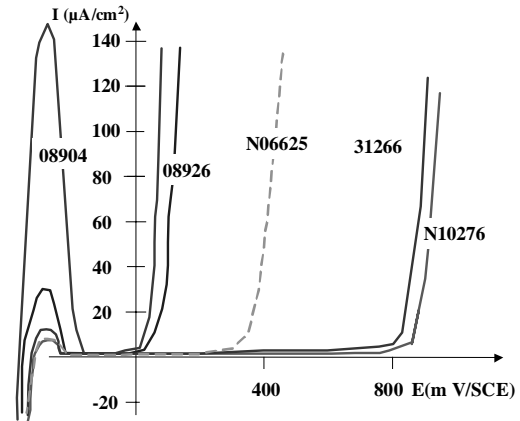


Fig4 - Polarization curves in NaCl 300 g/l, pH=1, 80°C/176°F

- Simulated Scrubbing Environment : the results of these tests [1] combined to CLI-FAFER research presented in this paper and in previous works [2,3] have been used to establish a material selection guide for slurry absorber environment (Fig. 5) and an other guide for other parts of FGD systems (Fig.6) excluding inlet ducts.

For slurry environment including spray pipes, absorber in the spray zone and slurry tank, the main parameters to be taken into account are pH, chloride concentration and temperature. At 55°C/130°F, 316L must be avoided since this material is very sensitive to pitting and crevice.

More alloyed stainless steels (PREN_W > 30) may be selected according to Fig. 5 ; in such conditions, pH and chloride content are determining parameters.

pH	CHLORIDE CONTENT (ppm)									
	10 000	20 000	30 000	40 000	50 000	60 000	70 000	80 000	90 000	100 000
7	S 31 726									
6.5			S 32 205	S 32 520		N08 926			S 31 266	
6										
5.5										
5	S 31 266					N 10 276				
4.5										
4										

Fig. 5 - Material selection guide for Absorber Slurry Environments, Temperature 55°C/130°F, Fluoride content < 50 ppm

At 80°C, all materials were found to be more or less sensitive to localized attack whatever the chloride content but among them, super-austenitics 08926 and 31266 and Ni base alloys with high Mo additions may be selected.

For other parts of FGD systems, the chloride content is generally lower but the medium may be more acidic due to H2SO3/H2SO4 rich condensates. When the raw gas is highly polluted by SO2/SO3, the pH of condensates may be very low (<1) so that highly alloyed materials have to be selected. In this case, high Mo containing Ni base alloys must be used.

		CHLORIDE CONTENT (g/l)												
		1			5			30			100			
F-(ppm)		0	400	1000	0	400	1000	0	400	1000	0	400	1000	
pH	6.5	316 L		317LMN			31803					31 266		
	4	31803 or 32 205			32205		32 520 or 08926 or 31266					31 266		
	2	32520 or 08926 or 31266						08 926 or 31266						
	1	N06022 / N10276												

Fig.6 - General material selection guide for FGD systems at 60°C/140°F vs Chlorides, pH & Fluorides

FIELD EXPERIENCE & CLI-FAFER REFERENCES

Field tests were carried out under care of NIDI and LaQue Centre for Corrosion for a multi-client programme. Samples fitted with multi-crevice washers were exposed to several field conditions in various FGD plants in USA and Germany. The results of this programme will be published elsewhere.

An example of the results gained after testing at Orlando Utilities, FL, USA is presented in Fig.7.

316L grade is obviously very sensitive to crevice corrosion. 317LNM and 31803 duplex are more resistant but they experienced some crevice. 6Mo super-austenitic (08926 type) is correctly resistant to crevice. Ni base alloy (N10276) is also very resistant to localized corrosion, but the total weight loss is slightly higher. This is probably the consequence of some transpassive dissolution due to the oxidizing power of the process conditions. Whatever, N10276 and N08926 were found quite satisfactory.

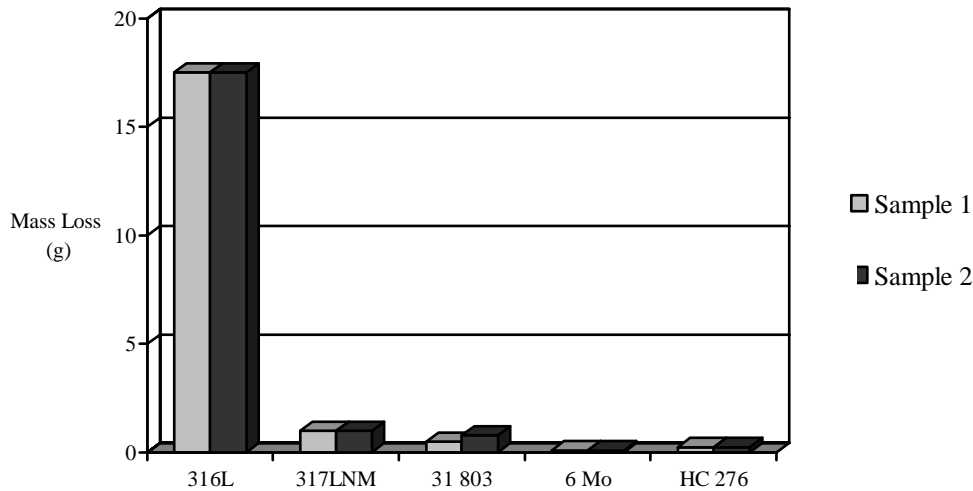


Fig. 7 - NIDI TEST PROGRAM, Orlando Utilities, Fl, USA
60,000 - 80,000 ppm Cl⁻, pH=5.5, 130F/55°C, 270 days

The main references for use of CLI-FAFER stainless steels and alloys in the world are mentioned below :

- S31726 : more than 2,000 metric tons (first order for Montana Power, Colstrip Units 3&4 in 1980)
- S31803 : more than 1,000 metric tons
- Super-Duplex S32520 : more than 4,000 metric tons were used for FGD systems since 1992 mainly in USA and Korea (first order in USA for TWA Cumberland)
- Super-austenitics : more than 3,500 metric tons (N08926, S 31 266 or S32050) mainly in Germany and Korea
- Ni base alloys : about 2,000 metric tons of clad plates since 1991

CONCLUSIONS

The corrosion properties of several stainless steels including super-austenitic and super-duplex materials have been investigated and compared to lower alloyed grades and to nickel base alloys in unwelded and welded conditions. Field tests were also carried out on some of these alloys.

From these tests, materials selection charts, taking into account the main process parameters like temperature, pH and chloride content were designed.

The super-duplex grade S32520 was found to be much more resistant than S31276 (austenitic) and S31803 (duplex) and close to 6 Mo grades up to 60°C/140°F. Combined to high mechanical properties and moderate cost, this super-duplex grade exhibits a very interesting performance to cost ratio.

Super-austenitic materials with Cr > 20% and Ni >23% with 5 to 6% Mo additions were found to be resistant up to about 80°C in slurry environments with high chloride concentration. More precisely, S32050 (SR50A) and S31266 (URB66) grades exhibit a better corrosion resistance than N06625 and 6Mo grade, close to Ni base alloys type N10276 and N06022. These good properties together with high mechanical characteristics make these alloys very promising for application in FGD systems.

REFERENCES

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